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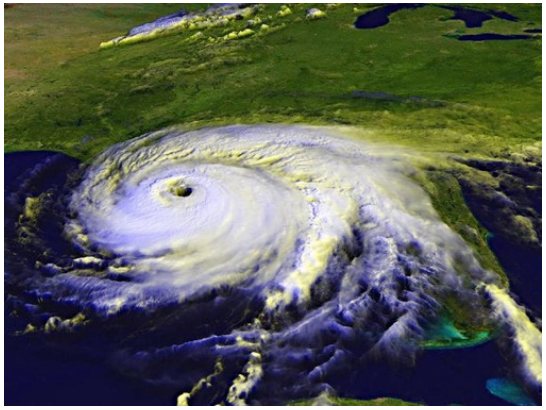

Chemically Mediated Redox Flow Batteries for Modular, High Power Energy Storage

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OFFICE OF ELECTRICITY DELIVERY & ENERGY RELIABILITY

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

LDRD LABORATORY DIRECTED RESEARCH & DEVELOPMENT

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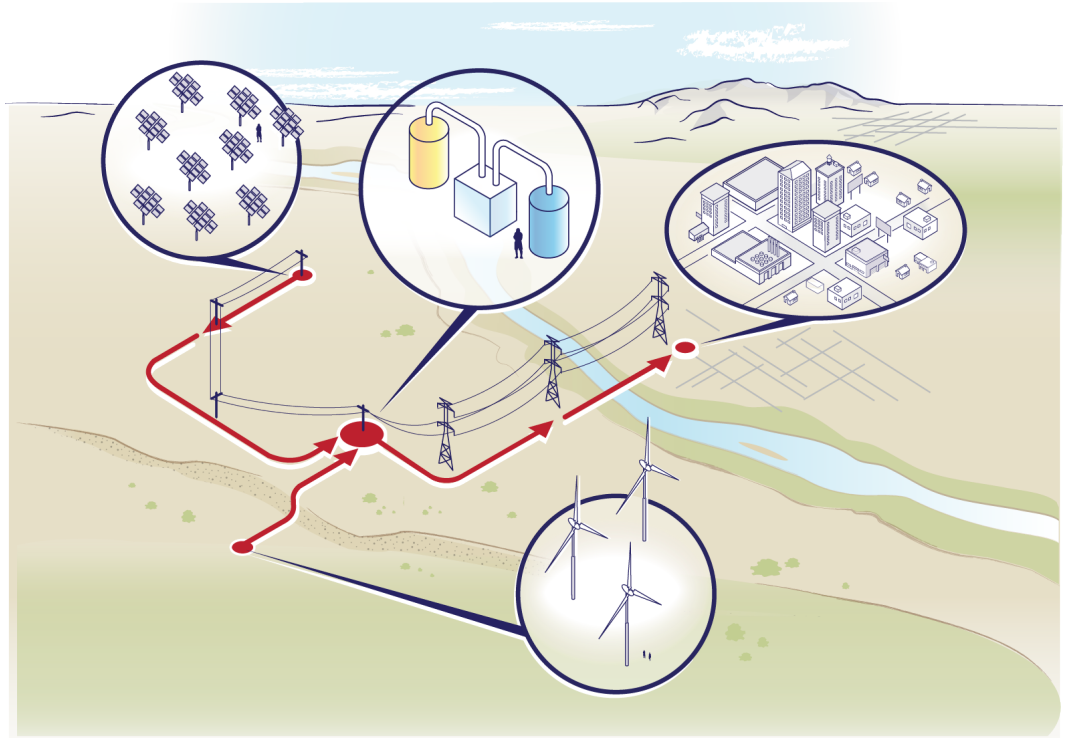
Motivation

Higher energy density redox flow batteries are needed for grid scale energy storage.

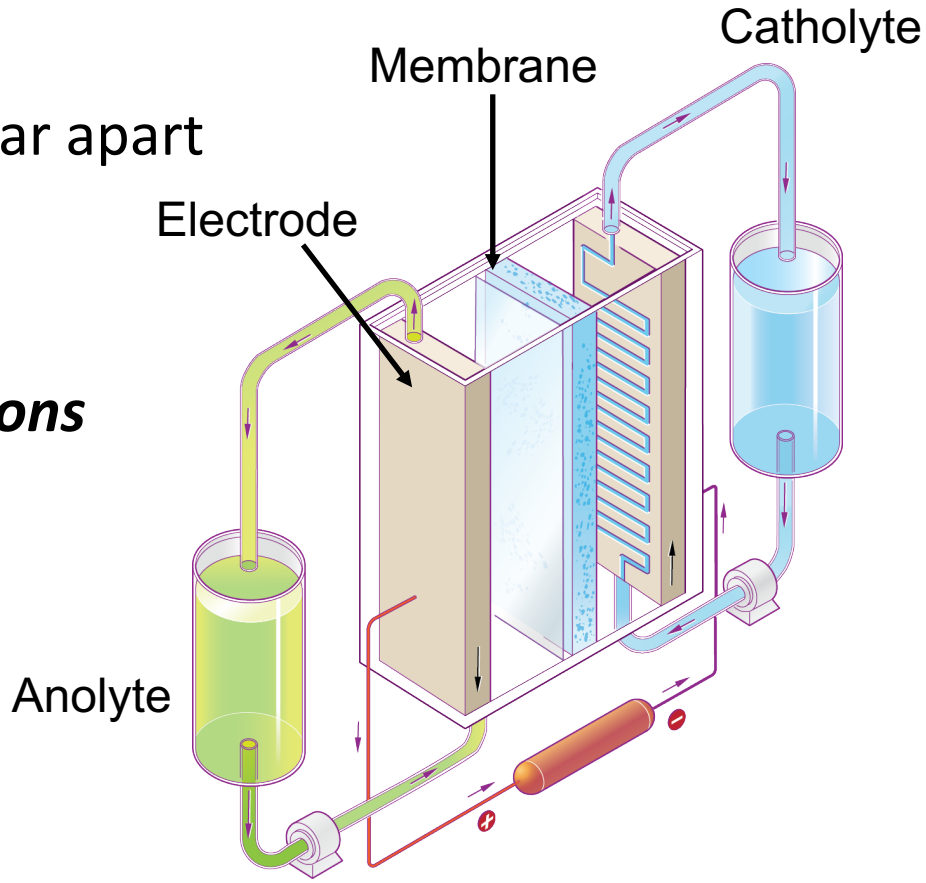
- Most flow batteries 25-100 Wh/L
- Li-ion battery 250-700 Wh/L
- Natural Gas 6,200 Wh/L



Traditional Flow Battery Architecture

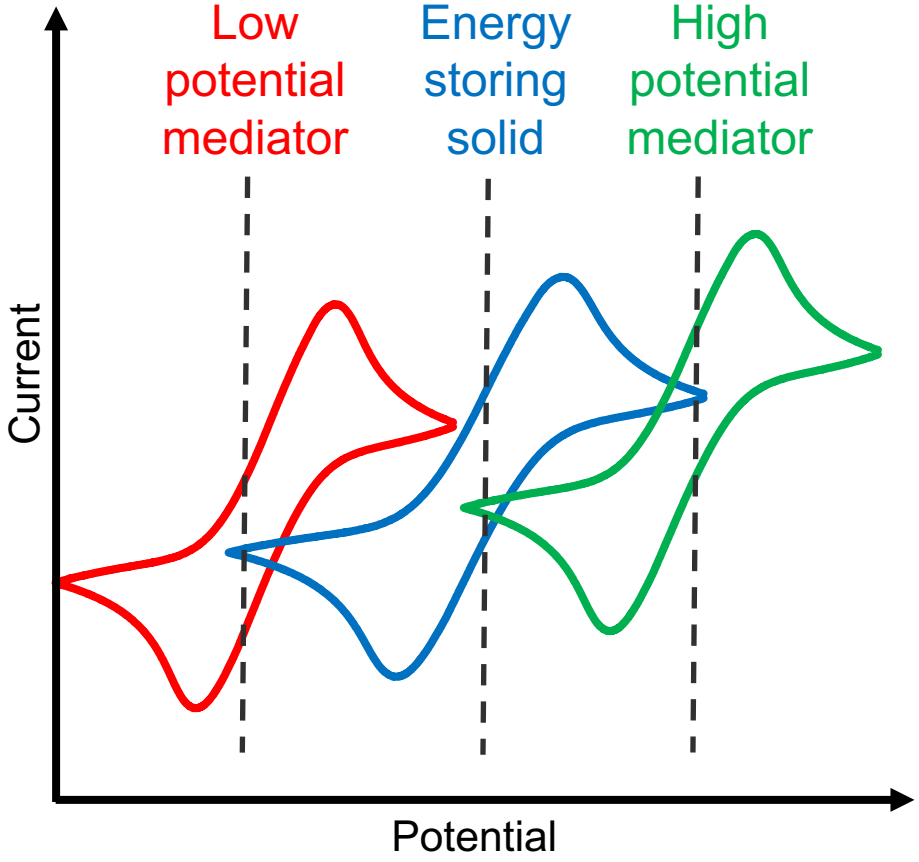
- Energy stored in large tanks
- Power determined by electrochemical cell
- Easily scalable
- Safe – reactants are located far apart

- ***Liquids limit design applications***
  - Flow rate
  - Viscosity
  - Cell design
  - Maximum energy density



What Is Mediation?

- Mediation uses soluble redox active species to oxidize and reduce solid energy storing materials.



Cathode Charge Reaction

At electrode in cell:

$Mediator \rightarrow Mediator^{+} + e^{-}$

In solution tanks:

$Mediator^{+} + Solid \rightarrow Solid^{+} + Mediator$

Cathode Discharge Reaction

At electrode in cell:

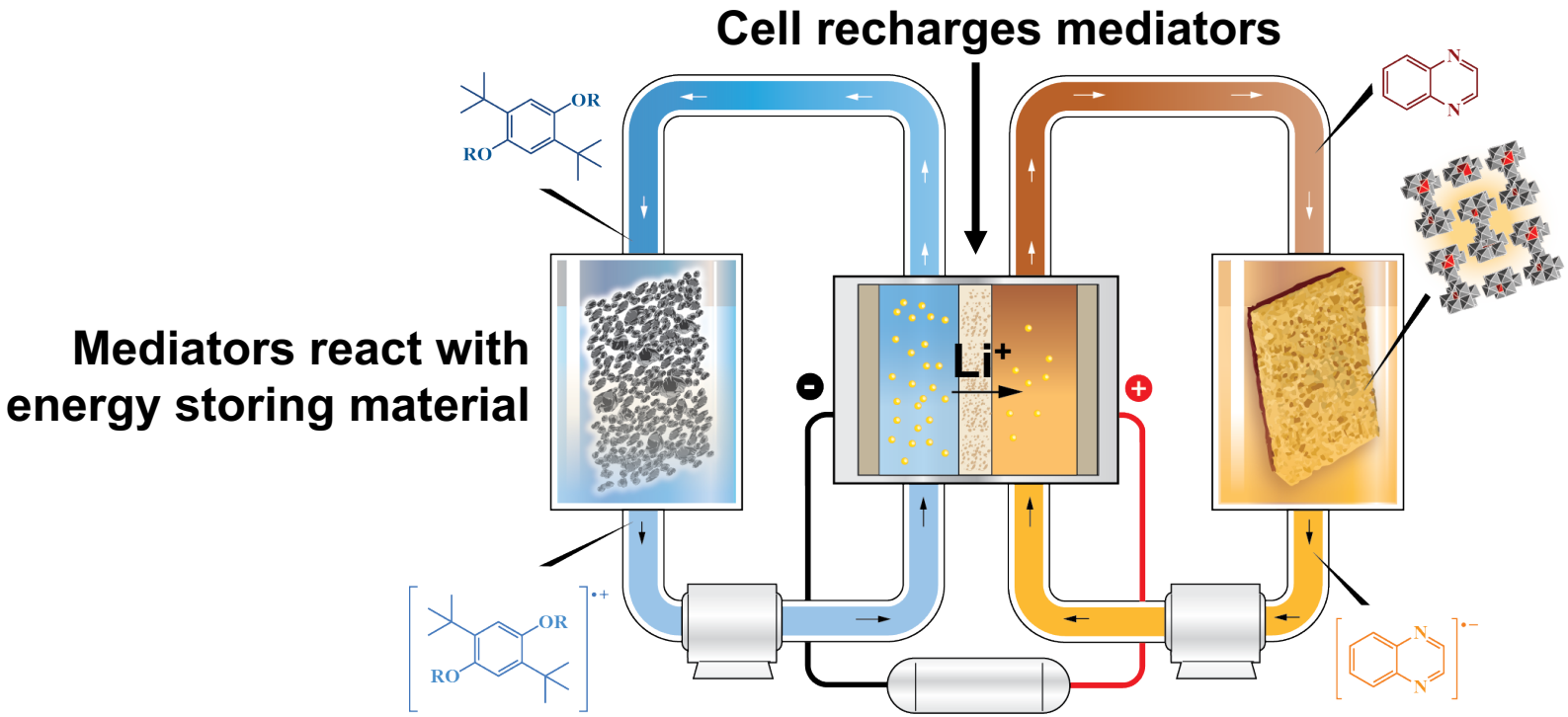
$Mediator^{+} + e^{-} \rightarrow Mediator$

In solution tanks:

$Mediator + Solid^{+} \rightarrow Solid + Mediator^{+}$

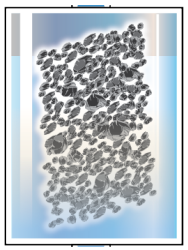
Mediation Applied to a Flow Battery

- Power Output
  - electrodes oxidize and reduce mediators at cell
- Energy Storage
  - mediators oxidize and reduce energy storing solid

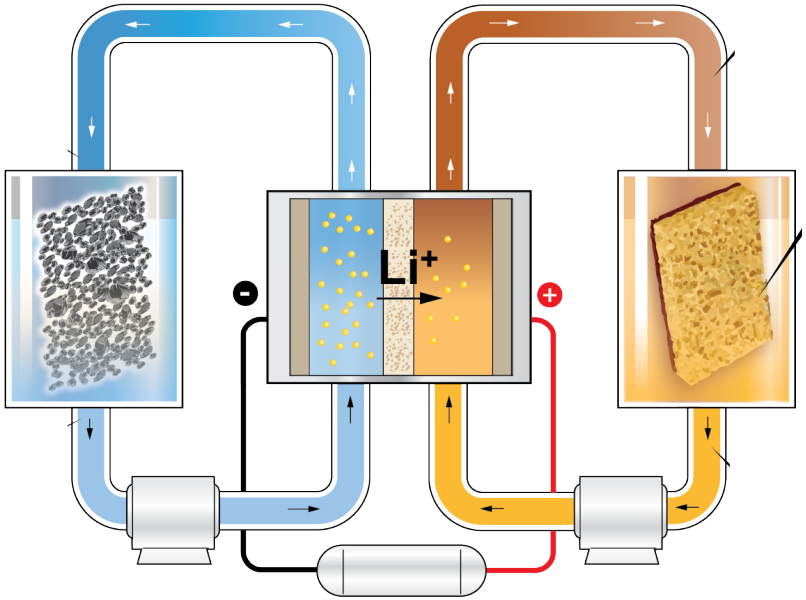


The Mediation "Dream"

- Energy density of Li-ion
- Scalability of redox flow battery
  - energy and power decoupled
- Safety of redox flow battery
  - anode and cathode far apart
- Rapid recharge by exchanging anode/cathode canisters

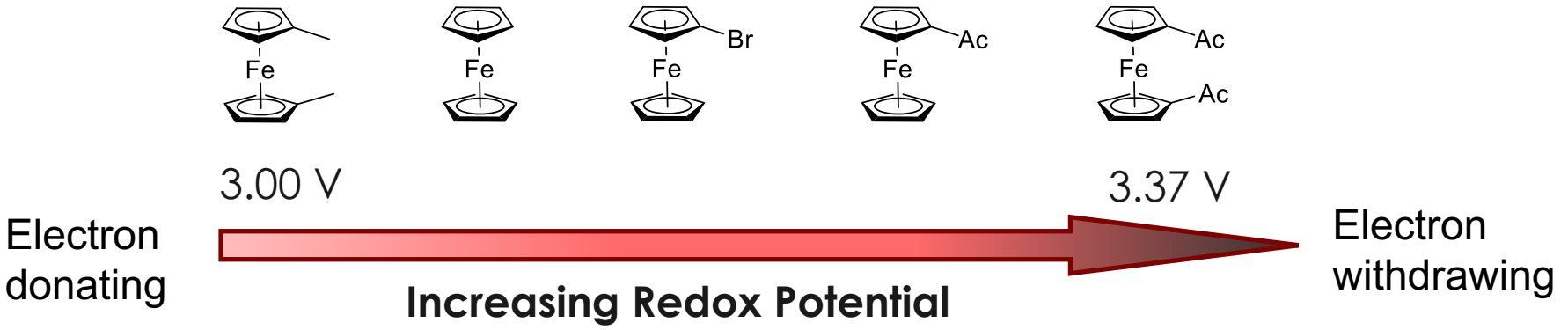


Swap canisters for fast recharge



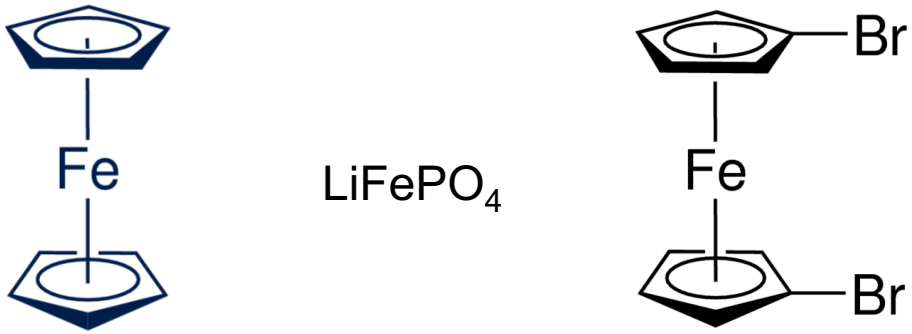
Mediation Offers Enhanced Design Flexibility

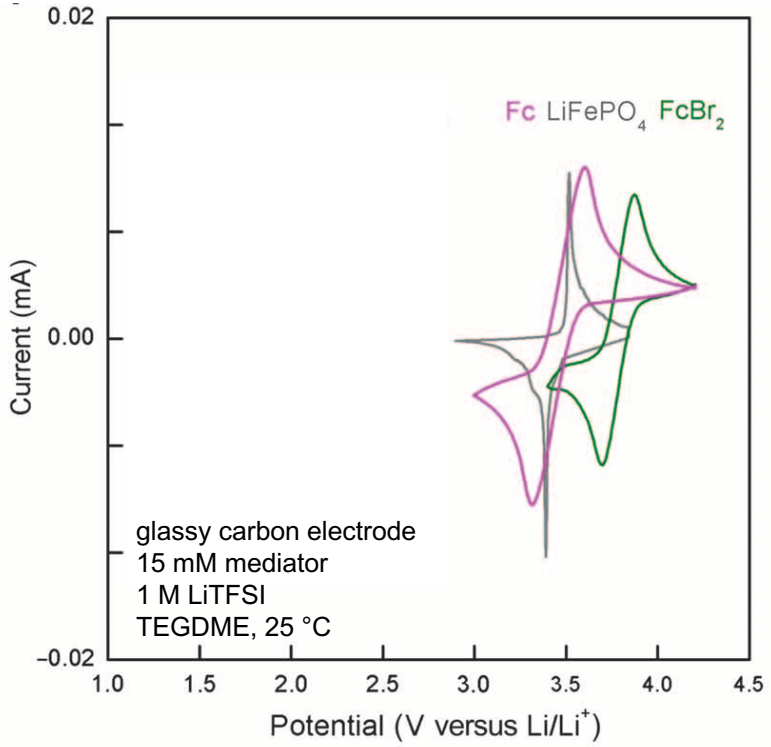
- Wide range of solvents possible
  - Optimize viscosity, temperature stability
- Solubility of energy storage material not concern
- Mediators can be low density, but high power
  - 500 mM should be sufficient
  - Large electrochemical libraries available



Li_xFePO_4 Cathode

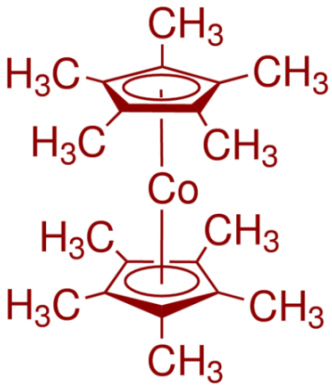
- Fc to reduce $FePO_4$
  - $Fc + FePO_4 + Li^+ \rightarrow Fc^+ + LiFePO_4$
- $FcBr_2$ to oxidize $LiFePO_4$
  - $FcBr_2^+ + LiFePO_4 \rightarrow FcBr_2 + FePO_4 + Li^+$





Li_xTiO_2 Anode

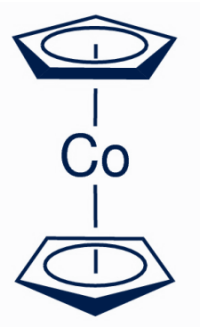
- Bis(pentamethylcyclopentadienyl)cobalt to reduce TiO_2
  - $CoCp^*_2{}^+ + 2TiO_2 + Li^+ \rightarrow CoCp^*_2{}^+ + 2Li_{0.5}TiO_2$
- Cobaltocene to oxidize $Li_{0.5}TiO_2$
  - $CoCp_2{}^+ + 2Li_{0.5}TiO_2 \rightarrow CoCp_2 + 2TiO_2 + Li^+$



1.67 V

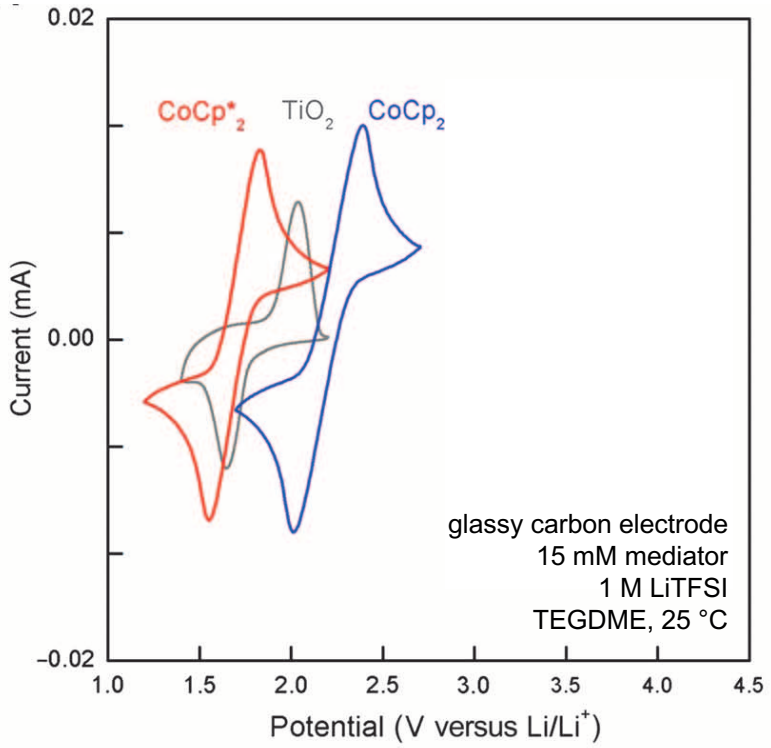
Li_xTiO_2

1.80 V



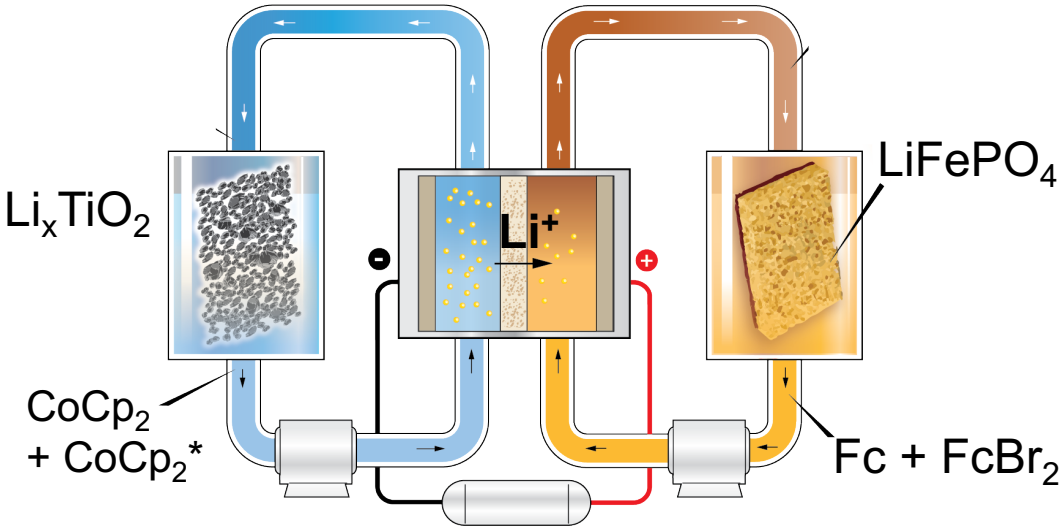
2.10 V

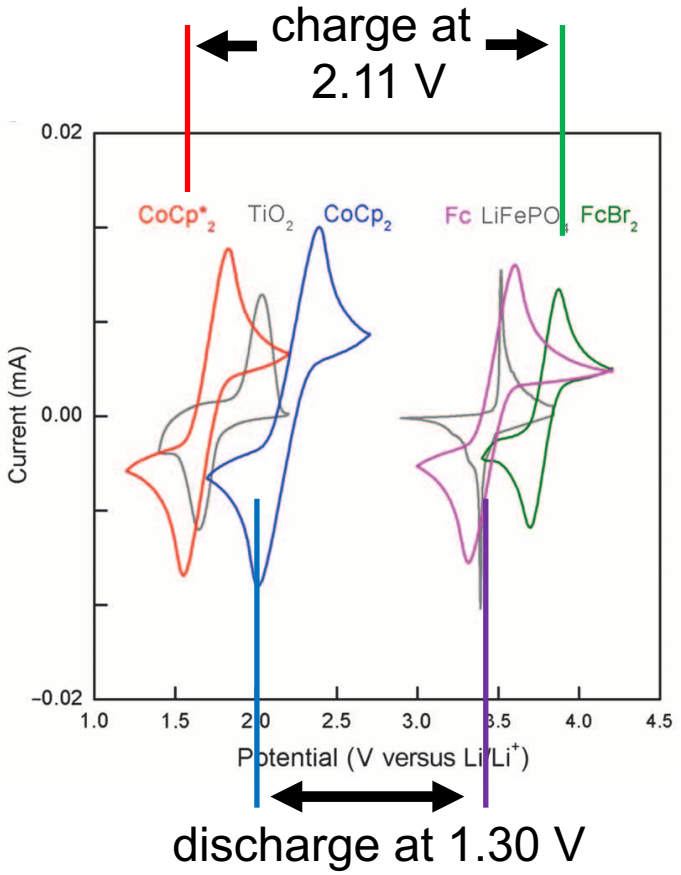
Potential vs. Li/Li^+



Li_xTiO_2 - Li_xFePO_4 Mediated Flow Battery

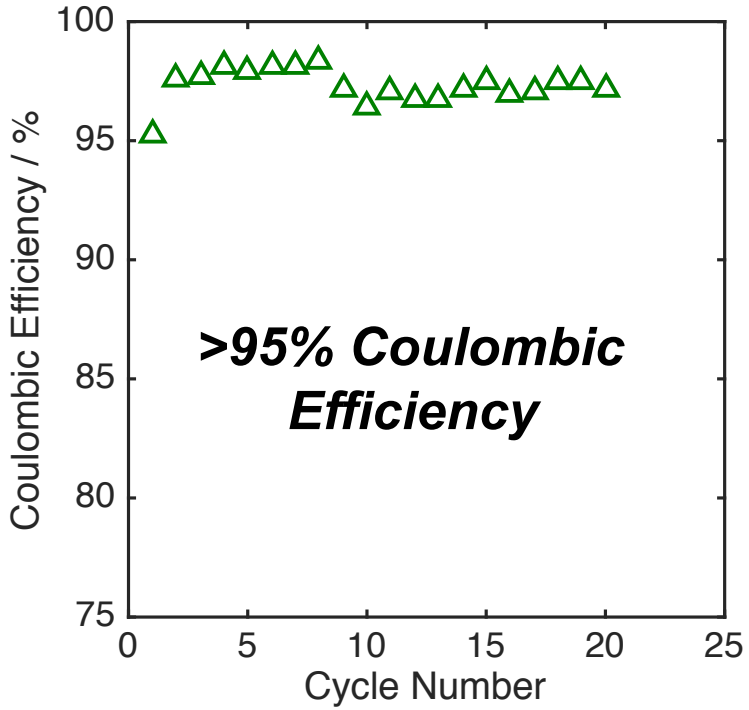
- Prove feasibility of literature chemistry by using larger scale
  - Electrolyte: 1 → 10 mL
  - Solids: 7 → 175 mg
  - Mediators 5 → 25 mM
  - Current density 0.09 → >1 mA cm^{-2}

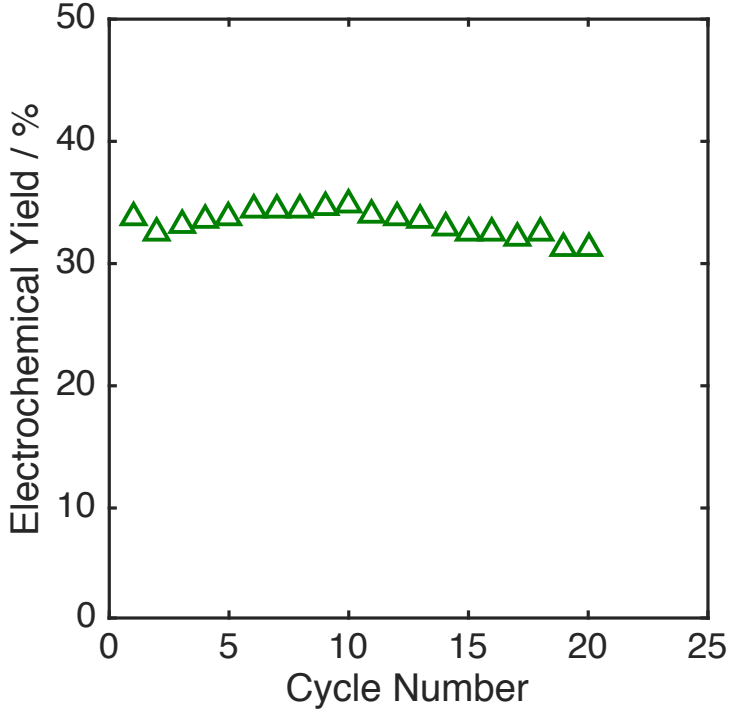




Mediated RFB Performance

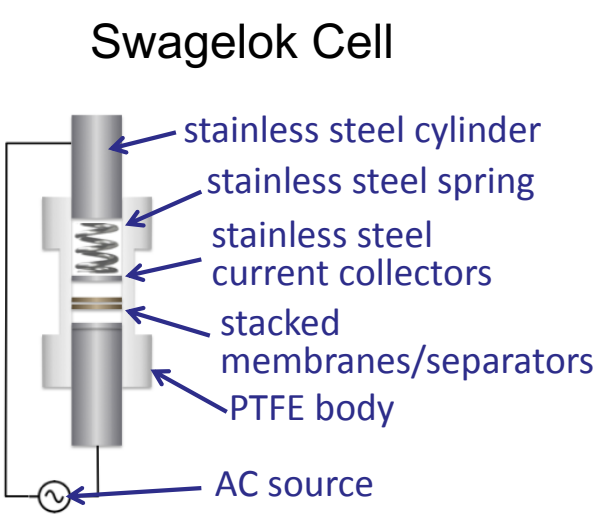
- Successful scale-up to 10 mL, 0.5 mA cm^{-2}
- >30% of maximum theoretical capacity ($Li_{0.5}TiO_2$)
  - Lower rates increase capacity
  - TiO_2 particle size vs. accessible capacity

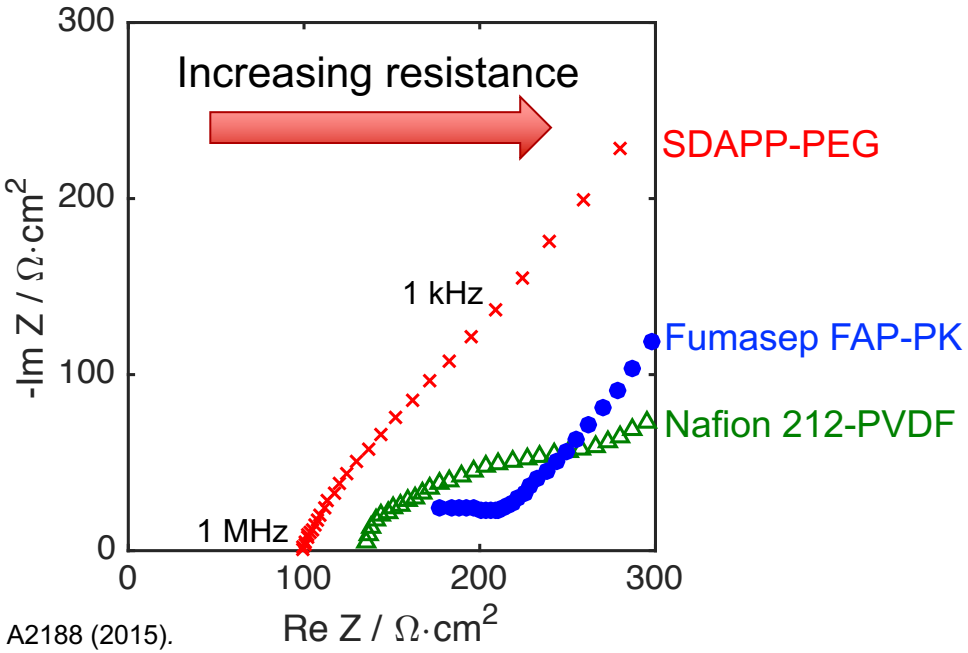




Membrane Choice Limits Performance

- Li-ion selective Nafion 212 – PVDF membrane is relatively high resistance
- Identify other membranes with lower resistance
  - Stack membranes in Swagelok cell and record impedance
  - SDAPP-PEG < Nafion 212-PVDF < Fumasep FAP-PK

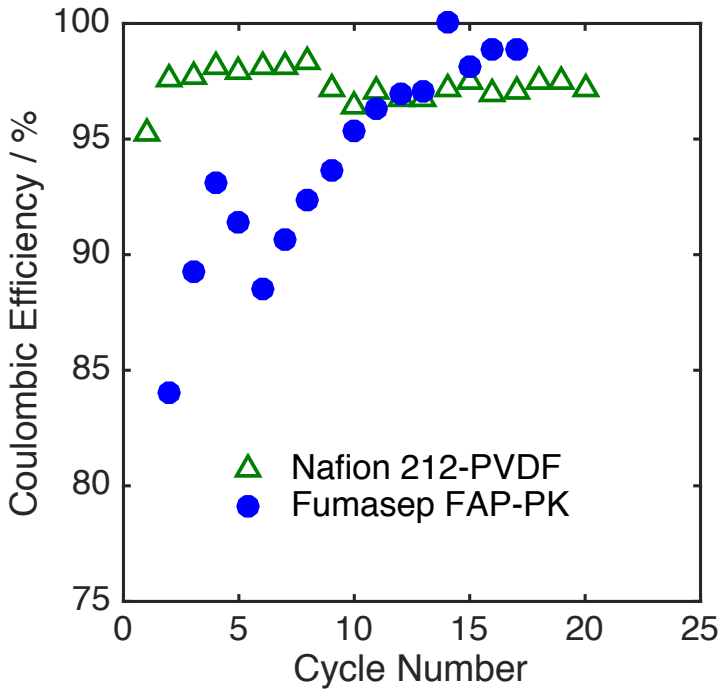


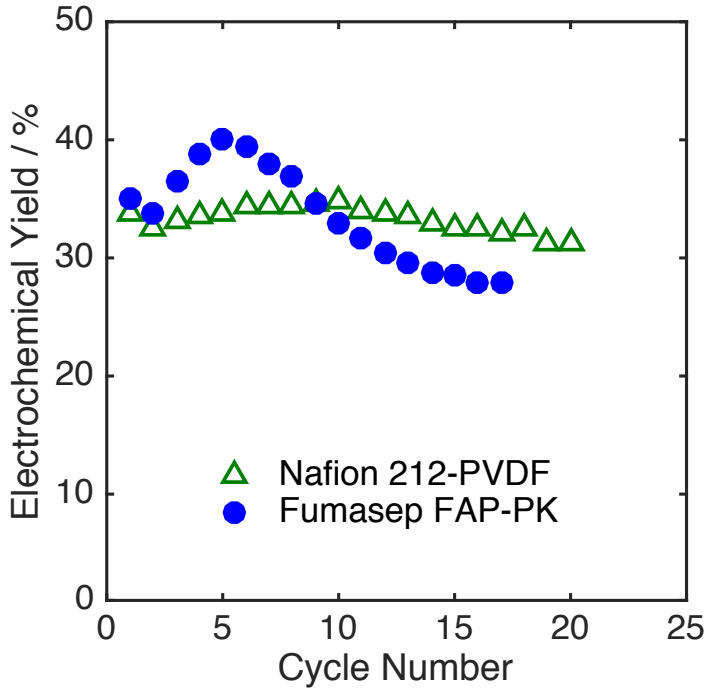


N.S. Hudak, L.J. Small, H.D. Pratt, T.M. Anderson, *J. Electrochem. Soc.* **162** A2188 (2015).

Conductive Membranes Enable Higher Current

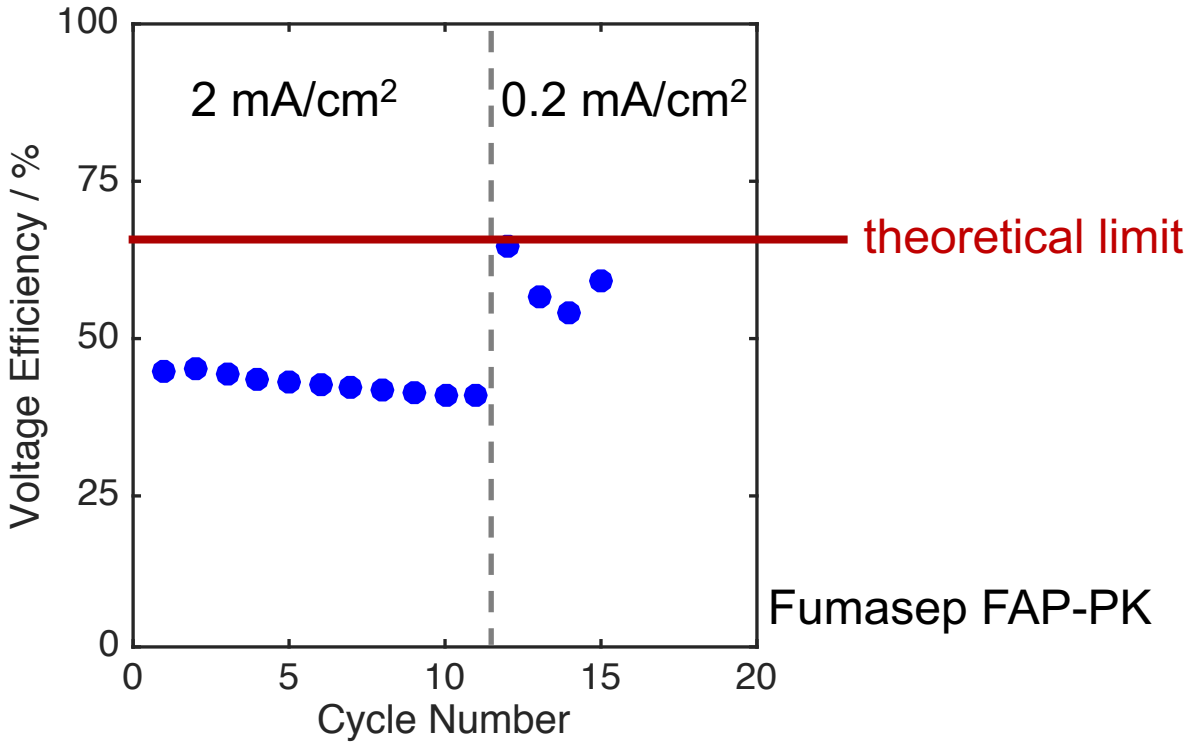
- Fumasep PK membrane enables 4x increase in current density over Nafion 212-PVDF (0.5 vs. 2 mA cm^{-2})
- More variable performance due to crossover





Voltage Efficiency Is Concerning

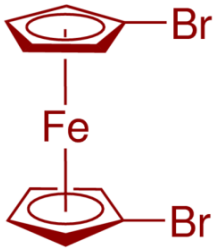
- Chosen mediators used overpotentials up to 0.3 V
  - 1.30 V discharge / 2.11 V charge = 61% voltage efficiency
- High overpotentials = low voltage efficiency



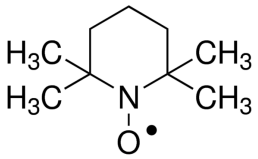
Influence of Cathode Mediator

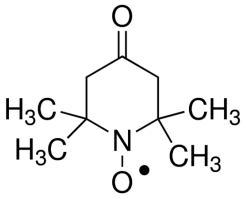
- Minimize mediation overpotential
- Maximize mediator solubility
- How does redox potential influence mediation rate?

Metallocenes

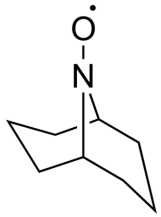


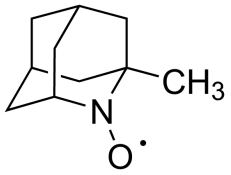
TEMPO

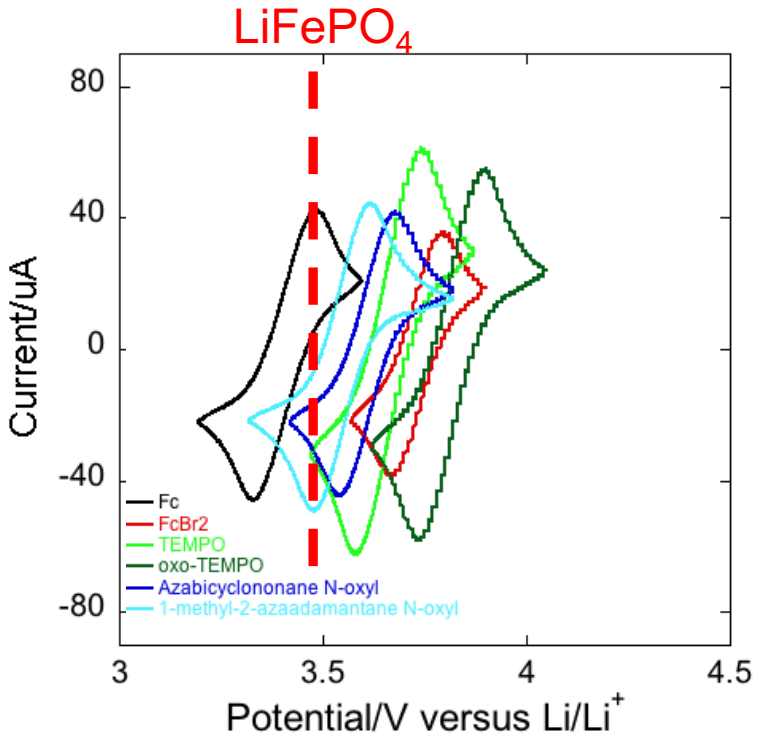




N-oxyl







Summary

- Mediated flow batteries are promising for modular, high density energy storage
- Mediation potentials must be optimized to increase voltage efficiency

- Path forward
  - Charge storage solids with higher surface area for faster mediation
  - Solvents optimized for mediator solubility and viscosity
  - Scalability of RFB
  - Optimize mediator : solids : electrode ratio

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Questions?

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